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Observation of singly ionized selenium vacancies in ZnSe grown by molecular beam epitaxy

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Electron paramagnetic resonance (EPR) has been used to investigate singly ionized selenium vacancy V_{Se}^+ centers in ZnSe epilayers grown by molecular beam epitaxy (MBE). The study included undoped and nitrogen-doped films. Spectra taken at 8 K and 9.45 GHz, as the magnetic field was rotated in the plane from [100] to [010], showed an isotropic signal at $g=2.0027\pm0.0004$ with a linewidth of 5.8 G. In the two samples where this signal was observed, estimates of concentration were approximately 1.1×10^{17} and 6.3×10^{17} cm^{-3} . The appearance of the EPR signal correlated with an increase in the Zn/Se beam equivalent pressure ratio (during growth) in undoped films and with an increase in the nitrogen concentration in doped films. We conclude that the singly ionized selenium vacancy may be a dominant point defect in many MBE-grown ZnSe layers and that these defects may play a role in the compensation mechanisms in heavily nitrogen-doped ZnSe thin films. © 1997 American Institute of Physics. [S0003-6951(97)02717-4]

Considerable effort has been focused in recent years on identifying and controlling the dominant point defects in ZnSe epilayers grown on GaAs substrates. A major goal of this work has been to increase the net acceptor concentration and thus permit efficient current-injection devices to be fabricated. Nitrogen is the most promising *p*-type dopant, but unwanted compensation centers have limited the maximum achievable carrier density to the low 10^{18} cm^{-3} level despite incorporation of nitrogen at levels as high as 10^{20} cm^{-3} . A review of this compensation problem in nitrogen-doped ZnSe films was recently published by Prior.¹

In the present letter, we describe the results of an electron paramagnetic resonance (EPR) study of two undoped and two nitrogen-doped ZnSe epilayers grown by molecular beam epitaxy (MBE). The signal we observe at $g=2.0027$ in two of the four samples is assigned to a singly ionized selenium vacancy (V_{Se}^+) center. Its presence correlates with an increase in the Zn-to-Se ratio in the undoped material and with an increase in nitrogen in the doped material. Our observation of large concentrations of singly ionized selenium vacancies in an undoped and a nitrogen-doped ZnSe epilayer provides experimental verification that these native defects may play a significant role in this material.

There have been several first-principles calculations^{2,3} of selenium vacancies in ZnSe, and there also have been several experimental studies,⁴⁻⁷ which invoked the presence of selenium vacancies to explain observed data in MBE grown ZnSe. Theoretical treatments have led to conflicting views on the role that selenium vacancies play. Laks *et al.*² concluded that the formation energy of the singly and doubly ionized selenium vacancies was so high that they did not play any important role in ZnSe, whereas Garcia and Northrup³ found that a very large lattice relaxation made the doubly ionized selenium vacancy the most abundant native point defect in *p*-type ZnSe. Experimentally, Hauksson *et al.*⁴ observed two distinct donor-acceptor pair recombination processes in a nitrogen-doped ZnSe epilayer and suggested that the deeper donor was a singly ionized ($V_{\text{Se}}-\text{Zn}-\text{N}_{\text{Se}}$) complex. In a related optically detected magnetic resonance (ODMR) study at 9.32 GHz, Murdin *et al.*⁵ observed three signals (at

$g=1.11$, 1.38, and 2.00) in two nitrogen-doped ZnSe films, and they assigned the $g=1.38$ signal to the deep donor ($V_{\text{Se}}-\text{Zn}-\text{N}_{\text{Se}}$)⁺ proposed earlier by Hauksson *et al.*⁴ Kennedy *et al.*⁶ extended the ODMR studies to higher microwave frequencies (24 and 35 GHz) and showed that the $g=2.00$ signal was anisotropic. In this latter investigation, the ODMR signal at $g=2.00$ was assigned to a deep donor comprised of a selenium vacancy paired with an impurity, most probably Cu or Ag believed to be present at concentrations less than 10^{15} cm^{-3} .

In our study, a Bruker ESP-300 spectrometer, operating at a microwave frequency of 9.45 GHz, a static-field modulation frequency of 100 kHz, and a microwave power of 5 mW, was used to obtain the EPR data. Glassware from an Oxford Instruments ESR-900 helium gas flow system extended through a standard rectangular TE₁₀₂ microwave cavity and maintained the sample temperature near 8 K. The microwave frequency was measured with a Hewlett Packard 5340A counter and the magnetic field was measured with a Varian E-500 digital gaussmeter. A small MgO:Cr crystal was used to correct for the difference in magnetic field between the sample and gaussmeter probe (the isotropic g value for Cr^{3+} in MgO is 1.9800).

The four ZnSe layers in this study were grown in a custom MBE system at West Virginia University. Two were undoped and two were nitrogen doped. The samples were grown at 300 °C on semi-insulating (100) GaAs substrates using high-purity (7N) elemental Zn and Se from conventional MBE sources (EPI). Prior to growth, the substrates were cleaned using atomic hydrogen. Different Zn/Se beam equivalent pressure (BEP) ratios were used when growing the two undoped films. One undoped ZnSe layer (referred to as sample A) was grown using a Zn/Se BEP ratio of 0.63 and the other undoped film (sample B) was grown using a BEP ratio of 0.46. The thicknesses were 1.7 and 1.6 μm for samples A and B, respectively. The two nitrogen-doped layers were grown using a Zn/Se BEP ratio of 0.49, but with drastically different nitrogen fluxes. The lightly doped film (sample C) was grown under a flux of molecular nitrogen and, based on photoluminescence data, is estimated to con-

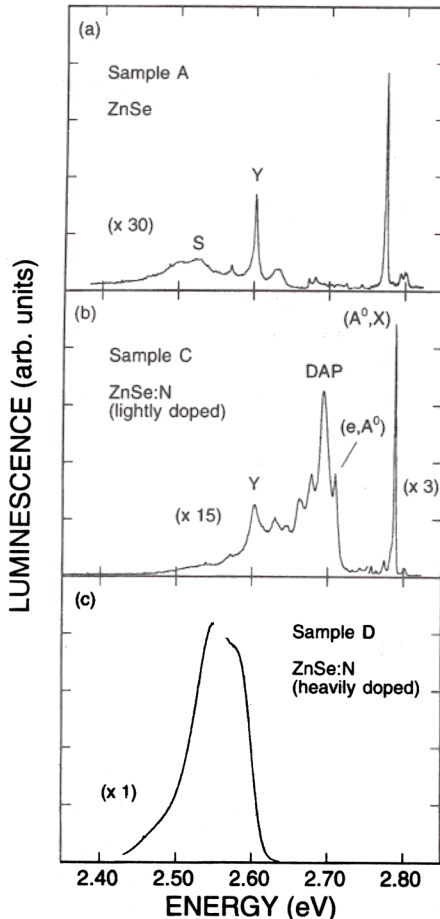


FIG. 1. Photoluminescence at 4.8 K from (a) sample A, (b) sample C, and (c) sample D. Portions of the PL spectra have been expanded by the factors indicated on the plots.

tain less than $1 \times 10^{17} \text{ cm}^{-3}$ atomic concentration of nitrogen. The more heavily doped film (sample D) was grown under an atomic nitrogen flux from a rf plasma source (Oxford CARS-25). Secondary ion mass spectrometry analysis showed that this latter film contains $1.5 \times 10^{19} \text{ cm}^{-3}$ nitrogen. In both cases, a $0.4 \mu\text{m}$ thick undoped ZnSe buffer layer was grown prior to the nitrogen-doped layer. Samples C and D had doped layers of thickness 1.3 and $1.8 \mu\text{m}$, respectively.

Before proceeding with the EPR measurements, liquid-helium photoluminescence (PL) was used to characterize the four samples. The data are shown in Fig. 1. A 325 nm HeCd laser was used for excitation and the incident power density was 1.7 W/cm^2 . The undoped films, samples A and B, had very similar PL spectra. A representative scan from sample A is shown in Fig. 1(a). These two samples exhibit a sharp bound exciton line at 2.7749 eV . The emission at 2.60 eV is the "Y" line and the broader band at 2.52 eV is the "S" band, as described by Dean.⁸ The PL from sample C, the lightly nitrogen-doped film, is shown in Fig. 1(b). This spectrum clearly shows evidence of the nitrogen substitutional acceptor center. The nitrogen bound exciton (A^0, X) line occurs at 2.7889 eV , while donor-acceptor pair (DAP) recombination occurs at 2.694 eV and electron-acceptor (e, A^0) recombination occurs at 2.710 eV . Several orders of phonon replicas are observed. The shallow donor participat-

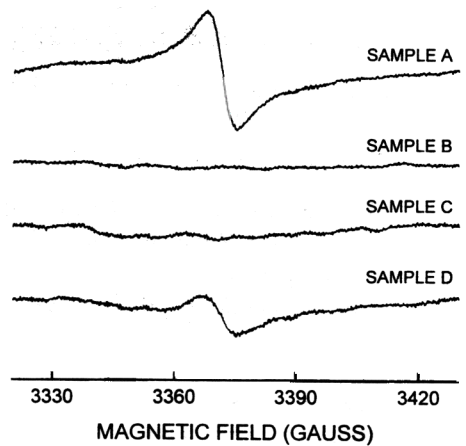


FIG. 2. Electron paramagnetic resonance spectra taken at 8 K and 9.45 GHz from four ZnSe epilayers.

ing in the DAP recombination is believed to be Ga or Cl. The PL from sample D, shown in Fig. 1(c), consists only of the characteristic broad band associated with heavy nitrogen doping in ZnSe films. Because the heavily doped sample has a much more intense emission, the spectra from samples A and C in Fig. 1 have been enhanced by the factors indicated.

The EPR data obtained from the four samples are shown in Fig. 2. These spectra were taken under identical spectrometer conditions and, except for slight variations in film volume, can be directly compared. The EPR samples, consisting of film and substrate, had nominal substrate dimensions of $0.5 \times 2 \times 5 \text{ mm}^3$ and were cleaved from larger samples. Because of the small volumes of these ZnSe films, this study required that the spectrometer be operated at maximum sensitivity to allow observation of small absolute numbers of paramagnetic defects. To enhance the signal-to-noise ratio, 20 scans were averaged. Spurious signals from the EPR cavity and sample holder, have been removed from the EPR data in Fig. 2 by subtracting a background spectrum of a similarly sized "bare" GaAs substrate.

An EPR line approximately 5.8 G in width and centered at $g = 2.0027 \pm 0.0004$ was observed in sample A (see Fig. 2). The concentration of paramagnetic defects represented by this signal is approximately $6.3 \times 10^{17} \text{ cm}^{-3}$. We do not know whether these defects are uniformly distributed throughout the film, or are localized within a portion of the film. This estimate of the defect concentration was obtained from the known sensitivity of the spectrometer (5×10^{10} spins for a linewidth of 1 G, a microwave power of 5 mW, and a temperature of 8 K). Samples B and C do not have an observable EPR signal (see Fig. 2) and this suggests that, if similar paramagnetic defects are present, their concentration is below the level of detectability (less than $4 \times 10^{16} \text{ cm}^{-3}$). Sample D does have an EPR signal that appears identical, except for intensity, to the signal in sample A. The concentration of paramagnetic defects represented by this signal is approximately $1.1 \times 10^{17} \text{ cm}^{-3}$. The intensity of the EPR signals in samples A and D did not change during illumination at 8 K by a HeCd laser (325 and 442 nm) or an argon ion laser (458 and 514 nm). Also, rotating the magnetic field from a direction perpendicular to the plane of the film to a direction lying in the plane of the film (i.e., from the

[100] to the [010] produced no change in the signals.

The isotropic EPR signal, observed in samples A and D, is assigned to the singly ionized selenium vacancy (V_{Se}^+). Our assignment is based primarily on the very small g shift ($\Delta g = +0.0004$) exhibited by the center. In general, singly charged anion vacancies in II–VI materials give rise to isotropic EPR spectra with g values close to that of the free spin. For example, the singly ionized anion vacancy occurs at $g = 2.0034$ in ZnS (Ref. 9) and at $g = 2.000$ in CdTe.¹⁰ In the alkaline-earth chalcogenides,¹¹ the singly ionized anion vacancy occurs at $g = 2.0033$ and 2.0036 in CaS and SrS, respectively, and at $g = 2.0030$ and 2.0032 in CaSe and SrSe, respectively. In contrast, shallow donors and acceptors with the unpaired spin centered primarily on an impurity usually have considerably larger g shifts. Also, the singly ionized zinc vacancy can be ruled out as the responsible entity since this defect in ZnSe has already been assigned¹² to an anisotropic EPR signal with $g_{\parallel} = 1.9548$ and $g_{\perp} = 2.2085$. The zinc interstitial in ZnSe has been assigned¹³ to an ODMR signal with $g = 1.9664$. Thus far, there has been no experimental evidence for the existence of isolated anion interstitials stable at room temperature in II–VI compounds.^{14,15} This leaves the selenium vacancy as the most viable candidate for the EPR signal observed in our epilayers.

Gorn *et al.*¹⁶ have previously reported an EPR signal from the singly ionized selenium vacancy in electron-irradiated bulk ZnSe crystals. They were able to resolve the hyperfine from the twelve closest selenium neighbors, but the hyperfine from the four nearest-neighbor zinc ions was not observed (because of a low signal-to-noise ratio). More importantly, they report a g value of 2.0085 for the singly ionized selenium vacancy in bulk ZnSe. This value, although similar, is measurably different from the 2.0027 value we are reporting. It is expected that the g value for the selenium vacancy would be the same in bulk and thin-film samples, thus making this difference in measured g values a matter of interest. Additional studies are needed to resolve this issue.

The observation of an EPR signal in sample A and not in sample B is consistent with the selenium vacancy assignment. During growth, the Zn/Se BEP ratio was measurably greater in sample A than in sample B and, thus, it is reasonable to expect more selenium vacancies might be present in sample A. It is also informative to compare sample D with samples B and C since these three samples have very similar Zn/Se BEP ratios. The observation of an EPR signal in sample D and not in samples B and C suggests that heavy nitrogen doping enhances the formation of Se vacancies.

The singly ionized selenium vacancy is a charged defect, and this requires that additional defects of opposite charge must be present to maintain overall charge neutrality in the samples exhibiting an EPR signal. In the case of the heavily doped material sample D, the necessary charge compensation is most likely provided by singly ionized nitrogen acceptors (N_{Se}^-). Nitrogen is present in this sample at a concentration of $1.5 \times 10^{19} \text{ cm}^{-3}$, and only about $1.1 \times 10^{17} \text{ cm}^{-3}$ are needed to compensate the observed EPR centers. The

identity of the charge compensating species is less obvious in the case of the undoped film sample A. Arsenic is a possibility since it could diffuse into the growing film from the GaAs substrate and form singly ionized acceptors (As_{Se}^-). The concentration of arsenic incorporated in the film would need to approach $6.3 \times 10^{17} \text{ cm}^{-3}$ in order to match the number of EPR centers in sample A. This arsenic concentration, although high, is not unreasonable and represents less than a monolayer of As at the substrate surface. In undoped films, the growth parameters that enhance the formation of selenium vacancies may simultaneously increase the diffusion of acceptor impurities from the substrate. The N_{Se}^- and the As_{Se}^- centers are not paramagnetic and, even if present, would not be observed in the EPR spectra.

In conclusion, we have observed an isotropic EPR signal with $g = 2.0027$ in ZnSe epilayers grown by MBE. We assign this signal to a singly ionized selenium vacancy (V_{Se}^+) and note that this defect can be present at significant concentrations in both undoped and heavily doped films. Our data suggest that these centers form more readily when a higher Zn/Se BEP ratio is used during growth. Also, the formation of selenium vacancies appears to be enhanced by heavy nitrogen doping. Although our focus has been on the singly ionized vacancy, both neutral and doubly ionized selenium vacancies may also be present in significant concentrations. These latter charge states are not paramagnetic and, thus, could not be monitored in the present EPR study. Our results strongly suggest that selenium vacancies may play a significant role in controlling the electrical properties of ZnSe epilayers grown by molecular beam epitaxy.

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